



Effect of Water on the Thermo-Mechanical Behavior of Carbon Cloth Phenolic

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Abstract

The results of thermo-mechanical experiments, which were conducted previously by one of the authors, are reviewed. The strain in the direction normal to the fabric plane was measured as a function of temperature for a variety of initial moisture contents and heating rates. In this paper, the general features of the thermo-mechanical response are discussed and the effect of heating rate and initial moisture content are highlighted. The mechanical interaction between the phenolic polymer and water trapped within its free volumes as the polymer is heated to high temperatures is discussed. An equation for the internal stresses which are generated within the polymer due to trapped water is obtained from the total stress expression for a binary mixture of polymer and water. Numerical solutions for moisture diffusion in the thermo-mechanical experiments were performed and the results of these solutions are presented. The results of the moisture diffusion solutions help to explain the effects of heating rate and moisture content on the strain behavior normal to the fabric plane.

Introduction

Carbon cloth phenolic (CCP) is a laminated, carbon fabric-reinforced phenolic matrix composite used as the thermal insulation in solid rocket motor nozzles. The CCP insulation protects the metallic structural components of the nozzle assembly from the high temperature exhaust gases during motor operation. In this application, CCP composites are exposed to very high surface heat fluxes. Flame surface temperatures are in the vicinity of 5000 °F and thermal gradients in excess of several thousand degrees per inch can develop within the CCP insulation. The high temperatures and severe thermal gradients sometimes result in localized material failures. The most common failure is delamination.

Delamination failures are the result of excessive interlaminar stresses within the CCP insulation. For a long time, the solid rocket motor community has sought an analysis tool which is capable of accurately calculating the interlaminar stresses in CCP insulation that are caused by the surface heat fluxes during motor operation. The magnitudes of the interlaminar stresses are dictated by several factors. Of particular significance is the thermo-mechanical behavior of the material in the direction normal to the fabric plane, the material direction which we shall refer to as the *ply-normal direction*.

The thermo-mechanical behavior of CCP is measured with the thermo-mechanical analysis (TMA) experiments. The TMA experiments are laboratory experiments, where specimens are heated at a constant heating rate and the dimensional changes are measured as a function of temperature. The strains which are measured in the TMA experiment are the result of the various chemical and physical processes which occur within the material as it is heated to high temperatures, such as thermal expansion, glass transition, moisture

desorption and thermal decomposition. In this paper, the term *thermal expansion* refers only to the volume increase which is associated with the thermally-induced increase in the amplitude of vibration of the polymer molecules about their equilibrium position. Thermal expansion is only one of the possible sources of strain which is measured in the TMA tests.

The thermo-mechanical behavior of the CCP in the direction normal to the fabric plane is significantly affected by the presence of moisture in the material. Moisture has two primary influences on the TMA response. First, water which is present in the material will lower the glass transition temperature. This effect has been reported by many previous authors (Refs. 1 to 5). The change from a hard, brittle behavior to rubbery behavior at glass transition is due to an increase in the mobility and the flexibility of the polymer segments. The intra-molecular bonds are primarily covalent bonds, while the intermolecular attractions are due to secondary bonding forces, which range from the weak van der Waals forces to the much stronger hydrogen bonds. The glass transition temperature is the temperature at which there is sufficient thermal energy to overcome the secondary forces between the polymer molecules and permit large-scale cooperative motion of the chain segments (Ref. 6). The absorption of moisture increases the distance between polymer molecules. This reduces the intermolecular forces between polymer molecules and reduces the thermal energy required for glass transition. Thus, the glass transition temperature is reduced.

The second effect of water on the TMA response is related to the hygrothermal stresses which are generated within the polymer upon heating. Water which is trapped inside the CCP material as it is heated to high temperatures can exert significant pressures. Pressurized water within the material will induce tensile stresses in the polymer network and a resulting increase in the strain response. These stress-induced strains can be a significant portion of the total strain which is measured in the TMA tests. Furthermore, these tensile stresses in the polymer may contribute significantly to delamination failures. As a result, it is necessary to determine the magnitude of these tensile stresses for any combination of moisture content and heating rate which may be experienced.

The objective of this paper is to discuss the role of moisture and moisture diffusion on the thermo-mechanical behavior as the CCP is heated to high temperatures. In the next section, we will review the results of previously-conducted TMA experiments that measured the effect of moisture content and heating rate on the strain response normal to the fabric plane. In the following section, we discuss the mechanical interaction between the phenolic polymer and water trapped within its free volumes as the polymer is heated to high temperatures. An equation for the internal stress which is generated within the polymer due to trapped water is obtained from the total stress expression for a binary mixture of polymer and water. Next, the results of a series of numerical solutions for moisture diffusion in the TMA experiments are presented. The diffusion solutions are performed for various initial moisture contents and heating rates. By comparing the predicted moisture content results with the measured strain results, we obtain a more thorough understanding of the interaction of water with the phenolic polymer and the effect of this interaction on the observed thermo-mechanical behavior. In this manner, we can start to formulate the essential ingredients of an analysis tool for calculating the interlaminar stresses in CCP insulation during motor operation.

Review of Ply-Normal Thermo-Mechanical Analysis Experiments

Stokes (Ref. 7) measured the effect of moisture content and heating rate on the ply-normal thermo-mechanical behavior of FM5055 carbon phenolic, a particular carbon phenolic made using 91LD phenolic resin. The carbon fabric was derived from rayon yarn supplied by Avtex Rayon. The tests were conducted on cylindrical specimens with a diameter of 0.25 in. and a length of 1.0 in. The specimens were fabricated so that the ply-normal direction is coincident with the specimen axial direction. The specimens were pre-conditioned to moisture contents of 2, 4.5, 6.1, 8.5, and 8.9 percent. Stokes (Ref. 7) measured the strain as a function of temperature as the specimens were heated at a constant rate of 2 and 10 °F/sec. The average strain response for each of the five initial moisture contents is shown in Figure 1. The results for a 2 °F/sec heating rate are shown in Figure 1(a) and the results for a 10 °F/sec heating rate are shown in Figure 1(b).

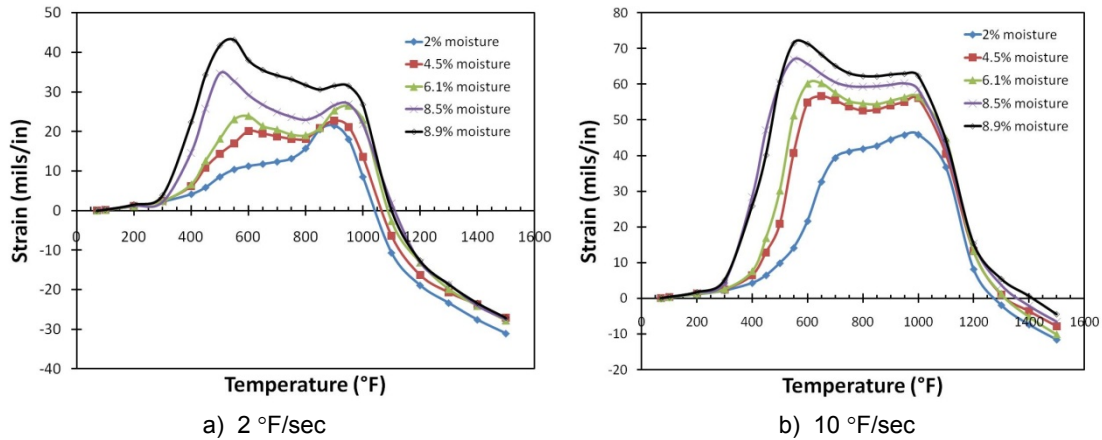


Figure 1.—TMA strain response normal to fabric plane versus temperature for specimens pre-conditioned to five initial moisture contents and heated at 2 and 10 °F/sec (from Stokes (Ref. 7)).
a) 2 °F/sec, b) 10 °F/sec.

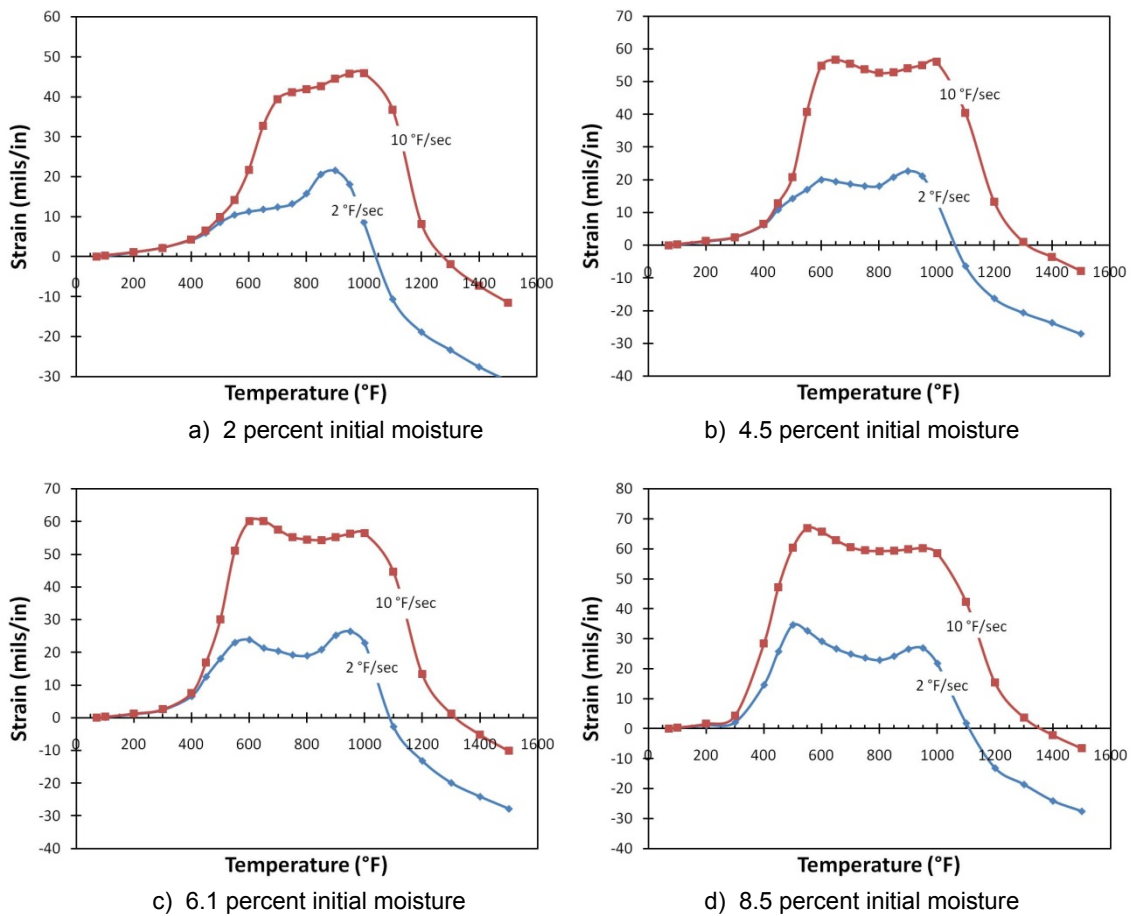


Figure 2.—TMA strain response normal to fabric plane versus temperature for specimens pre-conditioned to four initial moisture contents and heated at 2 and 10 °F/sec (from Stokes (Ref. 7)). a) 2 percent initial moisture, b) 4.5 percent initial moisture, c) 6.1 percent initial moisture, d) 8.5 percent initial moisture.

These same results are redisplayed in Figure 2 to illustrate the effect of heating rate. In each of the plots in Figure 2, the 2 and 10 °F/sec heating rate results are displayed for a specific initial moisture content. The results for 2, 4.5, 6.1, and 8.5 percent moisture are shown in Figures 2(a) to (d), respectively.

In addition to highlighting the influence of heating rate and initial moisture content on the thermo-mechanical behavior, the results shown in Figures 1 and 2 also serve to demonstrate the typical features of the thermo-mechanical behavior of carbon cloth phenolic normal to the fabric plane. At low temperatures, the strain curves are linear and the slopes of the curves are small. At these low temperatures, the polymer is in the glassy state and the strain is due solely to the thermal expansion of the glassy polymer. The coefficient of thermal expansion of the glassy polymer α_g is estimated from Figures 1 and 2 to be approximately $9 \times 10^{-6} \text{ }^\circ\text{F}^{-1}$.

The transition from glassy to rubbery behavior in the phenolic polymer occurs over a range of temperatures. The glass transition temperature T_g lies roughly at the center of this temperature range. As the glass transition temperature is approached, the strain curve begins to deviate from the initial linear portion of the curve. There is a sudden increase in the slope of the curve and a corresponding increase in the strain magnitude. The magnitude of the strain increase which follows glass transition is proportional to the initial moisture content and to the heating rate. Also, the temperature at which the glass transition begins to occur is dependent upon the initial moisture content; an increase in the moisture content causes the glass transition to begin at a lower temperature. However, the temperature at which glass transition begins does not seem to be dependent upon the heating rate, as this temperature is the same for the 2 and 10 $^\circ\text{F}/\text{sec}$ results for all four initial moisture conditions shown in Figure 2.

Notice that the TMA strain response for 4.5 and 6.1 percent moisture in Figure 1 appear to exhibit the same glass transition initiation temperature. The same is true for the 8.5 and 8.9 percent curves. A reasonable estimate of the glass transition initiation temperature for 2, 4.5, and 8.5 percent moisture is 400, 300, and 260 $^\circ\text{F}$, respectively. Using these values, the glass transition initiation temperature is plotted versus initial moisture content in Figure 3.

Most of the strain curves exhibit a double peak response. The first peak follows the glass transition and the second peak occurs at the onset of decomposition, within the range 800 to 1000 $^\circ\text{F}$. The temperature at which decomposition occurs appears to be dependent upon the heating rate. The decomposition temperature is shifted to higher values with an increase in the heating rate. This is to be expected since the decomposition process is a kinetic process and this behavior is characteristic of kinetic, temperature dependent processes.

There is a dramatic decrease in the strain following the decomposition peak. This decrease in strain is due to the volumetric shrinkage associated with the mass loss which occurs during polymer decomposition. The shrinkage strain remains fairly consistent for all initial moisture content conditions and both heating rates. This shrinkage strain has a value of 55 to 60 mils/in.

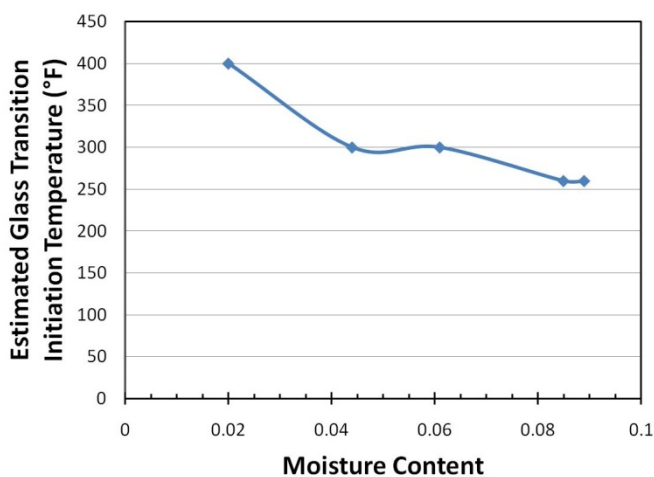


Figure 3.—Glass transition initiation temperature plotted versus initial moisture content, estimated from the TMA strain plots in Figure 1.

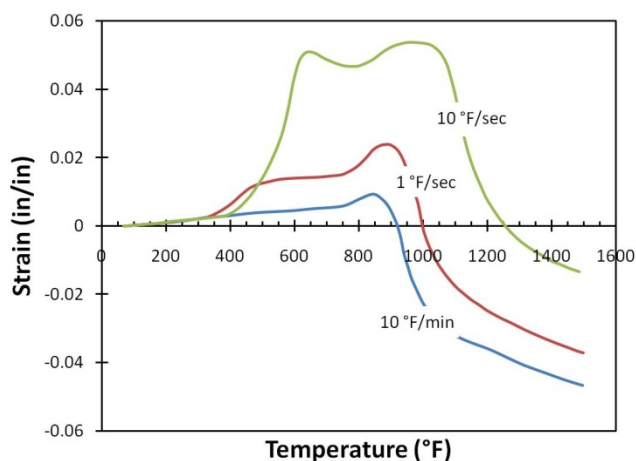


Figure 4.—TMA strain response normal to the fabric plane versus temperature for three heating rates (from Stokes (Ref. 8)).

There appears to be a permanent offset between the 2 and 10 °F/sec TMA response (Fig. 2). The strain curves for the higher heating rates are offset from the strain curves for the lower heating rates, with the higher heating rate curves having larger strain magnitudes. The strain offset appears to originate during the strain increase that occurs during glass transition. This indicates that there is considerable irreversible strain occurring within this temperature region. The value of the strain offset remains fairly constant even as the material is heated through polymer decomposition and charring. There is also a strain offset associated with two moisture content values (Fig. 1), but this offset is not as pronounced as the offset between the two heating rates.

The results shown in Figure 4 are taken from Stokes (Ref. 8) and further demonstrate the effect of heating rate on the thermo-mechanical response. These results were obtained using a cylindrical test specimen with a diameter of 0.25 in. and heating rates of 10 °F/min, 1 °F/sec, and 10 °F/sec. The initial moisture content in the test specimens was not reported. However, these specimens were tested in the as-received condition, which typically contains 3.5 to 4.5 percent moisture. By comparing the strain response in Figure 4 to the results shown in Figures 1 and 2, it appears that the initial moisture contents are in this same range of moisture contents.

The TMA response for the 10 °F/min heating rate does not seem to exhibit a glass transition behavior. The curve is linear from room temperature until the onset of polymer decomposition at approximately 800 °F. The slope of the curve below 800 °F is equal to the glass coefficient of expansion ($\sim 9 \times 10^{-6} \text{ } ^\circ\text{F}^{-1}$).

Notice that there is only one distinguishable peak in the 1 °F/sec TMA response. Like all the other strain curves, the strain is linear at low temperatures, with a slope equal to the glass coefficient of thermal expansion, and, at glass transition, there is a sudden increase in the slope and a corresponding increase in the strain magnitude. However, shortly after the glass transition, the slope becomes constant, with a value that appears to be approximately equal to the glass coefficient of expansion. The slope remains constant until the onset of decomposition. The strain curves shown in Figure 2 for a 2 percent initial moisture content exhibit a very similar strain behavior.

Mechanical Interaction of Polymer and Water in TMA Experiments

Many authors (Refs. 9 to 17) have speculated that absorbed water will exist within the polymer in two states: bound water and free water. Bound water molecules are immobilized and are attached to the polymer molecule by forming secondary bonds with hydrophilic groups such as hydroxyl groups in the phenolic polymer. Free water resides in the *free volume*, which are the unoccupied or “free” spaces between the polymer molecules. Free water is relatively free to travel throughout the free volume.

Denoting the free volume by V_f and the volume occupied by polymer molecules by V_p , the free volume fraction and polymer volume fraction is by definition $\phi_f = V_f/V$ and $\phi_p = V_p/V$, respectively, where V is the total volume given by $V = V_p + V_f$.

Some authors (Refs. 10, 12, 13, and 17) have suggested that the bound water disrupts the hydrogen bonds between the polymer molecules, causing swelling and increasing the mobility of the polymer segments. As a result, it is the bound water that is usually assumed to be responsible for the moisture swelling and the lowering of the glass transition temperature. The results of moisture swelling studies conducted by Stokes (Ref. 17) on carbon cloth phenolic composite specimens reveal a very low swelling efficiency, indicating that the majority of the absorbed water resides in the free volumes. Although we acknowledge the effect of bound water on the glass transition temperature, for the present study, we will assume that the water within the carbon phenolic specimens is primarily free water. The volume fraction of water is defined as $\phi_w = V_w/V$, where V_w is that portion of the free volume that is occupied by water molecules.

If moisture absorption in the phenolic polymer is an exothermic process, then by van 't Hoff's equation the equilibrium moisture content will decrease with an increase in temperature and water will be released as the material is heated (Refs. 18 and 19). Through various moisture conditioning and drying studies conducted on CCP, it appears that the equilibrium moisture content will be very small at temperatures not much higher than the boiling point of water. If the specimen is heated faster than the water can diffuse to an exterior surface and become liberated from the specimen, then the moisture content within the polymer will be in excess of the equilibrium moisture content. Under this non-equilibrium condition, the excess water, which is momentarily trapped within the polymer, exerts a pressure on the network of polymer molecules.

The driving force for the strain increase at glass transition is pressurized water within the free volumes of the polymer. The viscosity and Young's modulus of the polymer is significantly reduced at the glass transition due to an increase in the mobility of the polymer segments. The response to a large polymer network stress and a sudden drop in the Young's modulus and viscosity is the rather dramatic increase in strain which is observed as the glass transition temperature is approached.

In addition, it should be noted that, according to the *free volume theory*, the increase in the strain rate which occurs at glass transition is due to an increase in the free volume fraction (Refs. 3, 20, and 21). This can be written as $\alpha_r = \alpha_g + d\phi_f/dT$, where α_r is the slope of the strain curve in the rubbery state above glass transition. Thus, it may be stated more specifically that the increase in the slope of the strain response at glass transition is due to a volumetric straining of the free volume which is caused by pressurized water. Furthermore, since the strain increase at glass transition appears to be largely an irreversible strain, we must conclude that the increase in the free volumes is also largely irreversible.

In order to analyze the effect of water on the thermo-mechanical behavior, we will treat the polymer containing water as a condensed mixture of polymer and water, similar to the approach taken in Sullivan (Ref. 22). The total stress on the polymer/water mixture may be written as the sum of the contributions from the individual constituents, weighted according to the amount of volume that each constituent occupies. The total stress tensor may be written $\sigma_{ij} = \phi_w \sigma_{ij}^w + \phi_p \sigma_{ij}^p$, where σ_{ij}^w and σ_{ij}^p are the partial stress of water and polymer, respectively. The partial stress of water is written $\sigma_{ij}^w = -\delta_{ij} P_w$, where P_w is the partial pressure of water and δ_{ij} is the Kronecker delta function. The negative sign appears in the previous expression, since a positive increase in the water partial pressure will result in a negative increase (compression increase) in the total stress. Using contracted notation and denoting the direction normal to the fabric plane with the subscript n , the total stress in this direction is written

$$\sigma_n = -\phi_w P_w + \phi_p \sigma_n^p \quad (1)$$

The volume fractions of water and polymer may also be expressed as the product of the partial volume and partial density, $\phi_w = \rho_w v_w$ and $\phi_p = \rho_p v_p$. The partial density of water in the polymer/water mixture ρ_w is the mass of water per unit total volume of mixture ($\rho_w = m_w / V$) and the partial volume of water in the mixture v_w is the volume occupied by each gram of water ($v_w = V_w / m_w$).

Just as the pressure on a homogenous substance is dependent upon the temperature and its specific volume, the partial pressure of water in the mixture P_w is a function of the temperature and the partial volume v_w . The partial pressure is an increasing function of the temperature and it is inversely proportional to the partial volume. The variation of the partial volume v_w with temperature will be governed by the free volume of the polymer. That is, the volume that each water molecule occupies depends upon the amount of volume made available by the polymer network.

Since there are no mechanical restraints placed upon the specimen during the TMA test, the composite level stresses in the specimen are zero. In addition, the carbon fibers will not act to impart a restraining stress to the polymer/water mixture in the ply-normal direction. We can therefore set Equation (1) equal to zero and obtain $\sigma_n^p = (\phi_w / \phi_p) P_w$. Given that $\phi_w = \rho_w v_w$, we therefore have $\sigma_n^p \propto \rho_w v_w P_w$. Thus, the stress imparted to the polymer network in the ply-normal direction during the TMA tests is proportional to the amount of moisture in the specimen (ρ_w) and dependent upon the thermodynamic state of the water which defines the values of v_w and P_w at each temperature.

In the TMA specimen, it is expected that the partial volume of water will increase with temperature since water resides in the free volume and the free volume increases with the increase in strain above the glass transition temperature. The exact path of thermodynamic states that is traveled will depend upon the modulus and viscosity of the polymer network since these properties will determine how the free volume changes with temperature. This in turn will affect how the partial volume of water changes with temperature. At this point however, the partial volume of water and its variation with temperature cannot be quantified, since the relationship between the volume fraction of water ϕ_w and the free volume fraction ϕ_f is not known. We have only that $\phi_w \leq \phi_f$, based on our assumption that the majority of the water resides within the free volume.

The thermodynamic state of water in the TMA specimen is expected to be somewhat different from its thermodynamic state in the restrained thermal growth (RTG) experiment. Sullivan (Ref. 22) showed that, in the RTG experiment, water in the polymer free volumes is in a compressed liquid state and the thermodynamic state of the water traces a nearly constant volume path on a P-V-T diagram as the temperature is increased. Sullivan (Ref. 22) attributed this to the mechanical constraint placed on the specimens during the RTG experiment.

Moisture Diffusion in TMA Experiments

To help analyze the effect of water on the thermo-mechanical behavior shown in Figures 1, 2, and 4, numerical solutions for the moisture diffusion in the 0.25 in. diameter TMA specimens were performed. It was assumed that the diffusion of moisture in the TMA specimen could be simulated using Fick's first law with temperature-dependent moisture diffusivity. Fick's first law is written $\vec{J}_w = -\vec{D} \cdot \vec{\nabla} c_w$, where \vec{J}_w is the water mass flux vector, \vec{D} is a second-order tensor of moisture diffusivity coefficients and c_w is the moisture content, which may be written in terms of the partial densities as $c_w = \rho_w / (\rho_w + \rho_p)$.

Combining Fick's first law with the mass continuity equation $\partial c_w / \partial t + \vec{\nabla} \cdot \vec{J}_w = 0$ results in a transient moisture diffusion equation with c_w as the solution variable. The two-dimensional, axisymmetric form of the transient moisture diffusion equation was solved using ABAQUS (Ref. 23) (Dassault Systèmes

Simulia Corp.) and the DCAX4 mass diffusion elements. The boundary condition $c_w = 0$ was imposed on all external surfaces of the specimen.

During the TMA tests, moisture diffusion occurs in the plane of the carbon fabric and in the direction normal to the fabric plane. Previous moisture diffusivity measurements on carbon phenolic specimens indicate that the ratio of the moisture diffusivity in the in-plane and ply-normal directions can vary considerably (Ref. 24). In some cases, the moisture diffusivity in the ply-normal direction D_n was approximately equal to the value in the in-plane direction, while in other cases, the in-plane diffusivity D_f was several orders of magnitude greater than the ply-normal diffusivity. In order to address the potential effect of two-dimensional diffusion, we performed the numerical simulations using the following two extreme cases: 1) ply-normal diffusivity was set equal to zero ($D_n = 0$) and 2) the ply-normal moisture diffusivity was set equal to the in-plane diffusivity ($D_n = D_f$). The results indicate that moisture diffusion in the ply-normal direction had a negligible effect on the average moisture content in the TMA specimens. This is not surprising, since the cylindrical TMA specimen has a large length to diameter ratio (1.0/0.25). The amount of moisture that flows across the end surfaces will be a small fraction of the total moisture mass flow. All of the moisture diffusion results which will be presented in the following paragraphs were obtained from numerical solutions with $D_n = 0$.

It's common practice to express the variation of the moisture diffusivity with temperature using an exponential function of the form

$$D = D_o \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where D_o is the pre-exponential coefficient, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. It follows from this equation that a plot of the natural log of the diffusivity versus the inverse of the absolute temperature is a straight line with a slope of $-E_a/R$ and a y-intercept of $\ln D_o$.

In an attempt to determine the best approach for moisture conditioning carbon phenolic specimens, Stokes (Ref. 25) conditioned FM5055 carbon phenolic specimens in various relative humidity environments and at a handful of different temperatures and measured the moisture uptake or weight loss versus time profiles for each conditioning environment. Sullivan, et al. (Ref. 26) deduced the value of the in-plane diffusivity at each test temperature by performing numerical solutions for the moisture diffusion and comparing the numerical solution results with the weight loss/gain versus time histories measured by Stokes (Ref. 25). The values of the in-plane diffusivity at each test temperature which were obtained in Sullivan, et al. (Ref. 26) are shown as the individual data points in Figure 5. Note that the results are plotted as the natural log of diffusivity versus the inverse of the absolute temperature. A fairly good fit to the data ($R^2 = 0.960$) is obtained with the linear function using the values $D_o = 1.77 \times 10^6 \text{ in.}^2/\text{hr}$ and $E_a = 16.64 \text{ kcal/mole}$. This is shown as the solid line in Figure 5. The value of 16.64 kcal/mole for the activation energy compares well with the value obtained by previous authors for epoxy and epoxy composites (Refs. 2, 12, and 16).

In order to simulate the moisture diffusion in the constant heating rate TMA tests, the diffusivity must be continuously updated as the temperature is increased. At the end of each time step, the temperature was increased according to the time step increment and the heating rate. The moisture diffusivity was then updated using Equation (2) and the new temperature and the solution was performed for the next time step. This process was repeated until the conclusion of the simulation.

We performed a series of moisture diffusion solutions for a uniform initial moisture content of 2, 4.5, 6.1, and 8.5 percent and a heating rate of 2 and 10 °F/sec. The time incremental numerical solution yields the spatial distribution of the moisture content at each time step, and thus at each temperature. The moisture content distributions were used to calculate the volume average moisture content in the specimen at each time and temperature. The results of these numerical solutions are shown in Figure 6, where the average moisture content is plotted versus temperature. The 10 °F/sec results are plotted with

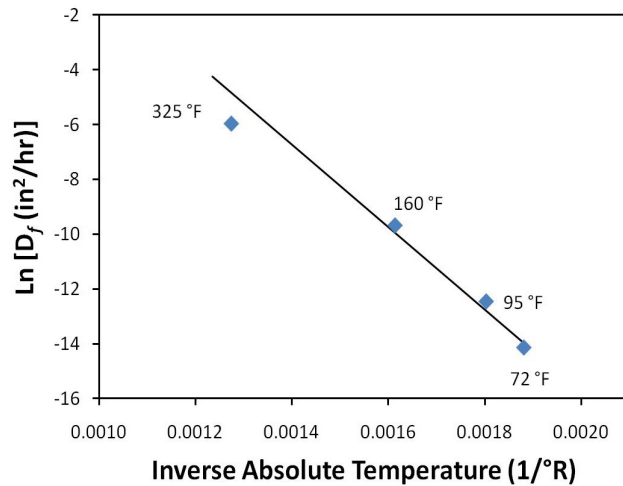


Figure 5.—Plot of natural log of diffusivity versus the inverse of the absolute temperature (from Sullivan, et al. (Ref. 26)).

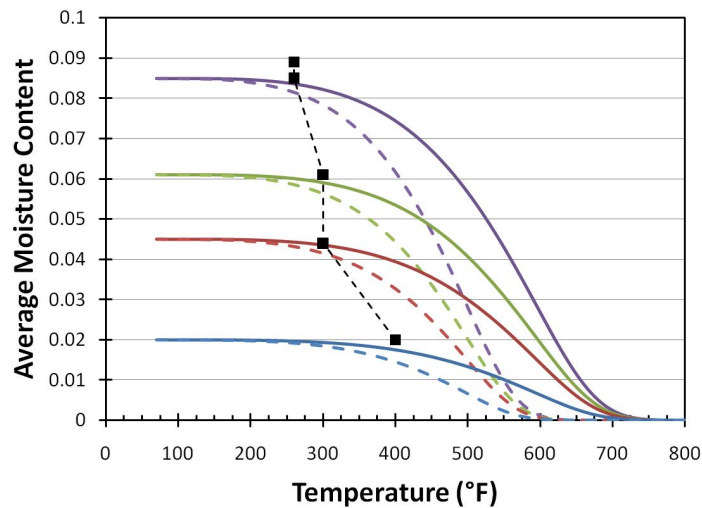


Figure 6.—Average moisture content versus temperature from numerical solutions of moisture diffusion in TMA specimens. Solid lines are 10 °F/sec results and dashed lines are 2 °F/sec results. Also plotted is moisture content versus the estimated glass transition initiation temperature from Figure 3.

solid lines and the 2 °F/sec results are plotted with dashed lines. We have also included the estimated glass transition initiation temperature versus initial moisture content (dashed black line) which was shown previously in Figure 3. In Figure 6, this is plotted with temperature as the abscissa.

The results in Figure 6 show that, for both 2 and 10 °F/sec heating rates, there is not a significant amount of moisture diffusion prior to reaching the glass transition initiation temperature and thus the moisture content for the 2 °F/sec specimen is roughly the same as for the 10 °F/sec specimen. These results are consistent with the thermo-mechanical behavior shown in Figure 2, where it was observed that the glass transition temperature was not affected by the heating rate. Recalling that the glass transition temperature is dependent upon the moisture content, we would not expect the glass transition temperature to be dependent upon the heating rate, since, prior to the glass transition temperature, the moisture content is not dependent upon the heating rate.

There are significant differences between the 2 °F/sec results and the 10 °F/sec results after the glass transition. In comparing two specimens that start with the same initial moisture content, the specimen which is heated at the higher rate will contain more moisture than the specimen heated at the slower rate at temperatures above the glass transition initiation temperature.

The relationship between moisture content and the TMA strain response is illustrated by the composite plots in Figure 7. The predicted moisture content and the measured strain are plotted versus temperature for 2, 4.5, and 8.5 percent initial moisture content and heating rates of 2 and 10 °F/sec. Again, the plot of glass transition initiation temperature versus moisture content from Figure 3 is included. The temperature at which the average moisture content curve intersects the plot of moisture content versus the estimated glass transition initiation temperature should coincide with the temperature at which the TMA strain response begins to exhibit glass transition behavior. This appears to be approximately true for all cases shown in Figure 7.

As the specimen is heated past the glass transition, the increase in strain occurs simultaneously with moisture diffusion. At this point, the 2 and 10 °F/sec predicted moisture content curves begin to diverge. As the difference between the two moisture content curves increases, the 2 and 10 °F/sec strain curves also begin to diverge. The higher heating rate results in a larger strain since there is more moisture present at any given temperature and since the polymer network stress is proportional to the amount of moisture in the specimen. Larger polymer network stresses lead to higher strain rates and higher cumulative strains.

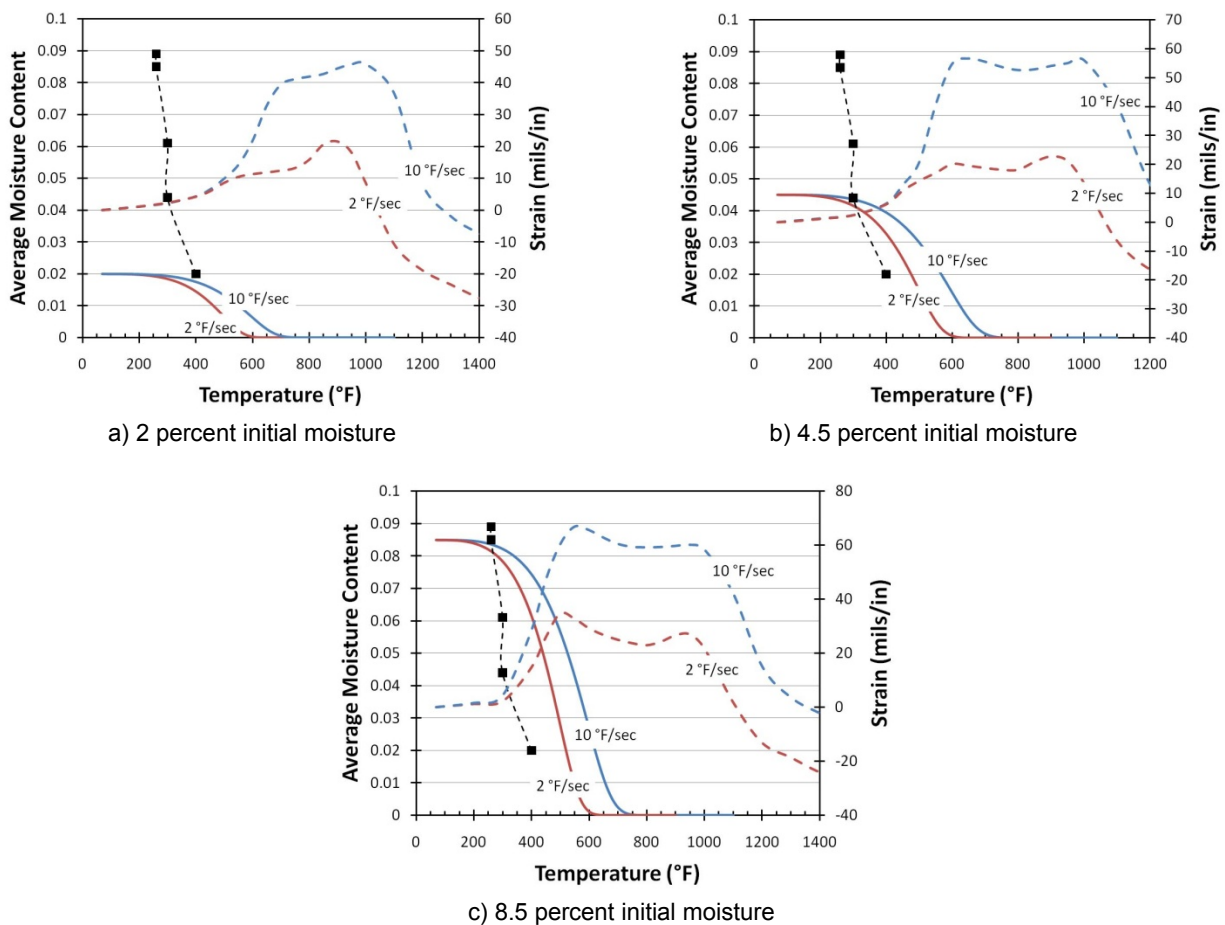


Figure 7.—Composite plots of predicted average moisture content (solid lines) and measured strain (dashed lines) versus temperature for heating rates of 2 and 10 °F/sec. The plot of moisture content versus glass transition initiation temperature is also included. a) 2 percent initial moisture. b) 4.5 percent initial moisture. c) 8.5 percent initial moisture.

For the strain curves with a double peak behavior, the temperature of the first peak is the temperature at which the polymer network stress σ_n^p becomes so small that it cannot produce any additional strain in the polymer network. The polymer network stress becomes small due to the effusion of moisture from the specimen. There is also a decrease in the partial pressure of water due to the increase in the free volumes which accompanies the strain increase. Although at this point, the relative magnitude of the latter effect is not certain. As the polymer stress becomes small, any elastic strain that was stored in the polymer network is recovered. Notice that for the 4.5 and 8.5 percent results, the temperature at the apex of the first peak in the thermo-mechanical response coincides with the temperature at which the predicted moisture content approaches zero. For the 2 percent results, the strain curve does not have a distinct first peak. In this case, the temperature at which the predicted moisture content approaches zero coincides with the temperature at which the slope of the strain curve decreases and returns to the glass coefficient of expansion α_g .

We also performed a series of moisture diffusion solutions for heating rates of 10 °F/min, 1 °F/sec and 10 °F/sec to help explain the thermo-mechanical behavior shown in Figure 4. In these simulations, the specimen heated at 10 and 1 °F/sec was assumed to have an initial moisture content of 3 and 4 percent, respectively. These initial moisture contents were chosen based on the apparent glass transition initiation temperature which is evident from the strain curves in Figure 4. Since the 10 °F/min strain curve does not exhibit an obvious glass transition behavior, we were not able to deduce the glass transition initiation temperature and estimate the initial moisture content. For the 10 °F/min simulation, we assumed initial moisture contents of both 3 and 4 percent.

The results of these numerical solutions are shown in Figure 8, where the predicted moisture content and strain response are plotted versus temperature. We have again included the estimated glass transition initiation temperature versus moisture content which was shown previously in Figure 3. For a heating rate of 10 °F/min, the predicted moisture content curve will not intersect the plot of glass transition initiation temperature versus the moisture content until temperatures above 500 °F, at which point there is no moisture left in the specimen. This is true whether the initial moisture content is 3 or 4 percent. This would explain the strain behavior for the 10 °F/min heating rate, which is linear from room temperature until the onset of decomposition with a slope equal to the glass coefficient of expansion α_g . Since the moisture has left the specimen before the glass transition temperature is reached, there would be no appreciable increase in the free volume and we would not expect an increase in the strain rate above that of the glass coefficient of thermal expansion.

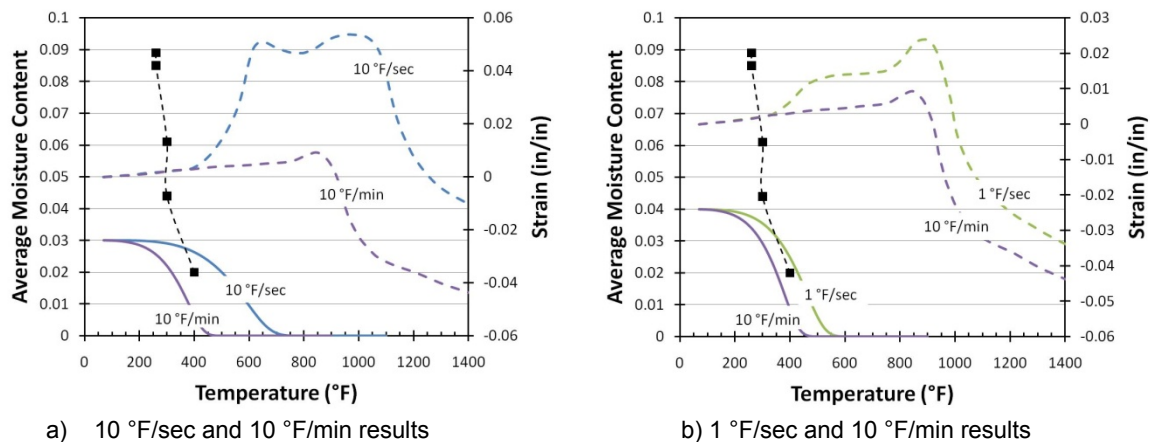


Figure 8.—Composite plots of predicted average moisture content (solid lines) and measured strain (dashed lines) versus temperature for heating rates of 10 °F/min, 1 °F/sec, and 10 °F/sec. The plot of moisture content versus glass transition initiation temperature is also included. a) 10 °F/sec and 10 °F/min results. b) 1 °F/sec and 10 °F/min results.

The moisture diffusion solution results also help to explain the thermo-mechanical behavior in the 1 °F/sec heating rate results. In view of the predicted moisture content results shown in Figure 8, it appears that, for 1 °F/sec heating rate, glass transition would begin in the vicinity of 400 °F and that the moisture will have evaporated from the specimen at temperatures slightly above 500 °F. This is consistent with the measured thermo-mechanical behavior, where the glass transition begins at temperatures just under 400 °F and the slope of the strain curve becomes constant and equal to the glass expansion coefficient α_g at approximately 500 °F. Although the material may experience a glass transition and become rubbery at 400 °F, if there is no water left in the specimen above 500 °F, there will be no partial pressure to cause an increase in the free volumes. We would therefore expect the strain response above 500 °F to have a constant slope equal to the glass coefficient of expansion.

Concluding Remarks

The presence of water in carbon cloth phenolic composites plays a significant role in the thermo-mechanical behavior normal to the fabric plane. The amount of water determines the glass transition temperature, the temperature at which the mechanical behavior of the polymer transitions from glassy to rubbery. Water is also a major source of strain as the material is heated above the glass transition temperature. The amount of water which is in excess of the equilibrium moisture content will exert a stress on the polymer network and the magnitude of this stress is proportional to the amount of excess water. There are indications that the polymer network stress produces both elastic and inelastic strains. The response to a large polymer network stress and a sudden drop in the Young's modulus and viscosity is the rather dramatic increase in the strain which is observed at glass transition. Thus, the amount of water within the polymer determines the temperature at which the rapid rise in strain is observed and the magnitude of this strain increase.

In this paper, we proposed to use a moisture diffusion model which is based on Fick's law with a temperature dependent diffusivity to simulate the moisture diffusion in the TMA experiments. The results of the moisture diffusion solutions help to illustrate the interaction of water and polymer and its effect on the various features of the thermo-mechanical response. For example, the analysis results reveal why the glass transition temperature is not a function of the heating rate. In addition, the results indicate that an increase in the strain rate will not occur at the glass transition temperature if there is no moisture remaining in the specimen when the glass transition temperature is reached. If there is no water left at glass transition, then the strain rate will be the same as the glass thermal expansion coefficient, even though the modulus and viscosity may have decreased dramatically at glass transition.

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14. ABSTRACT The results of thermo-mechanical experiments, which were conducted previously by one of the authors, are reviewed. The strain in the direction normal to the fabric plane was measured as a function of temperature for a variety of initial moisture contents and heating rates. In this paper, the general features of the thermo-mechanical response are discussed and the effect of heating rate and initial moisture content are highlighted. The mechanical interaction between the phenolic polymer and water trapped within its free volumes as the polymer is heated to high temperatures is discussed. An equation for the internal stresses which are generated within the polymer due to trapped water is obtained from the total stress expression for a binary mixture of polymer and water. Numerical solutions for moisture diffusion in the thermo-mechanical experiments were performed and the results of these solutions are presented. The results of the moisture diffusion solutions help to explain the effects of heating rate and moisture content on the strain behavior normal to the fabric plane.					
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